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Short communication

Promotion of anodic electron transfer in a microbial fuel cell combined with a silicon solar cell

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HIGHLIGHTS

- A traditional MFC and a silicon solar cell (SSC) are combined to build a novel MFC–SSC.
- Cell performances are significantly promoted by the SSC in MFC–SSC.
- Anodic microbial oxidation of organic substrate is enhanced in MFC–SSC.
- The SSC is compatible to promote the whole system without influencing anodic microbial reactions.
- Cooperation of anodic microorganisms and SSC improves electron transfer efficiency in the MFC–SSC.

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ABSTRACT

This study focuses on the promotion of electron transfer in microbial fuel cells (MFCs) by equipping a silicon solar cell (SSC) into the circuit. As compared to a sole MFC, a significant improvement of power output is observed in the MFC–SSC, that the maximum power density increases from 7.5 W m^{-3} –19 W m^{-3} by 2.53 times. A linear relationship between anodic potential and current has been observed when the current is below the limiting point of SSC. We estimate the electron transfer rate can be promoted in a MFC–SSC under the condition that the anodic microbial reactions are unaffected by the incorporation of a SSC. In this way, the anodic electrons are fully pumped and enter into the external circuit. This estimation is thereby demonstrated by the 24-h test, which shows the quantity of the electrons fluent in the circuit of a MFC–SSC is doubled and the microbial oxidation efficiency is improved to 341.6% as compared with a sole MFC.

1. Introduction

Microbial fuel cell (MFC) is a well-known bioelectrochemical device mainly used for power generation and contaminant remediation [1–4]. The efficiency of a MFC is influenced by many factors, such as electricigens, electrode material, electron donor and accepter species, equipment configuration, et al. [5–7]. In essence, all these factors are correlated with electron transfer processes. For examples, electricigens controls electrons transfer from organic substrates to anode electrode, and cathodic materials affect electrons transfer from cathode electrode to electron acceptors. Therefore, optimizing those factors to accelerate electron transfer rate would eventually improve the performance of MFCs [8]. Among those electron transfer processes, the anodic microbial electron transfer is critical to the whole MFC performance [9], principally because all electrons are produced from the oxidation of anodic "fuels" by microorganisms. Various methods have been applied to promote the microbial electron transfer rate, such as inoculating mixed microbial community, adding electron mediators, replacing electrode materials and optimizing electrode and cell design [10–13]. Specially, applying a potentiostat to fix the MFC's anode potential at a constant value was demonstrated to be an effective method to improve the electron transfer efficiency from microbes to anode [14,15]. However, it caused extra electric energy consumption, which is contradictory to the primary intention of operating a MFC in a cost-effective way.

Silicon solar cell (SSC), which is a stable, low cost and commercialized power generation device, can transform solar energy into electric energy. We previously found the combination of MFC with SSC could provide higher power output [16]. However, it has been so far unclearly known such a power promotion was achieved by what mechanisms. Moreover, the issues about the compatibility of SSC with MFC, the influences of SSC on anodic

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microorganisms of MFC, and the cooperating mechanisms of MFC with SSC were not discussed before. In this study, we optimized the MFC–SSC system by taking into consideration of the compatibility of SSC and MFC. In order to explore the electron transfer mechanisms, the performances of a sole MFC, a sterilized MFC–SSC and a MFC–SSC were compared in terms of power output, potential variation, anodic substrate oxidation efficiency and electron transfer efficiency. By virtue of the simple configuration and good performance, the MFC–SSC was believed to be highly applicable in practical fields of clean energy production and environmental remediation.

2. Experimental

2.1. Experimental setup construction and operation

A single-chambered MFC was used in this study, which was a U-shaped glass reactor with inner diameter of 5 cm and volume of 120 mL for each side. Both of anodic and cathodic electrodes were carbon felt (Sanye Carbon Co., Ltd, Beijing, China) of 0.5 (in thickness) × 10 (in width) × 10 (in length) cm^3 with 9 cm distance from each other. The cell was filled with a medium based on PBS, which contained 10.31 g L^{-1} $Na_2HPO_4{\cdot}12H_2O$, 3.31 g L^{-1} $NaH_2PO_4{\cdot}2H_2O$, 0.31 g L^{-1} NH_4Cl, 0.13 g L^{-1} KCl, 1.64 g L^{-1} CH_3COONa and 0.25 g L^{-1} yeast extract. The initial pH of the medium was 7.0 ± 0.2.

The anode was inoculated with anaerobic activated sludge (10% in volume ratio) which was collected from Gaobeidian Wastewater Treatment Plant (Beijing, China). It had been cultured for 1 month to make a stable biofilm attachment on the carbon felt. The cathodic chamber was slowly bubbled with sterile air to supply dissolved oxygen as electron acceptor. All experiments were carried out at 32 ± 2 °C to keep the microbial activity.

A commercial SSC and a resistor were in series connected with a MFC. The SSC's positive terminal was connected with the MFC's anode and the SSC's negative terminal was connected to the resistor and the MFC's cathode. A Xeon lamp with a UV and IR filter (PLS-LAX500, Trust Tech Co., Ltd, Beijing, China) was used as the light source and placed away from the SSC surface at a distance of 1 m. The illumination area of the SSC was 0.4 × 0.4 cm^2. When the illuminating intensity reached 1.8 mW cm^{-2}, the SSC could be fully activated and provide an open circuit voltage (OCV) at about 600 mV and a maximum current at about 3.3 ± 0.1 mA with an internal resistance of 20 Ω. Decreasing the illuminating intensity resulted in the part inactivation of SSC with an extreme large internal resistance, which would inevitably affect the performance of the cell system. Therefore, the illumination intensity was fixed at 2 mW cm^{-2} to ensure SSC can be fully activated and kept stable in the MFC–SSC system.

For all experiments, a MFC, a MFC–SSC and a MFC–SSC with sterile anode (called "sterilized MFC–SSC") were operated in parallel for performance comparison.

2.2. Electric data collection and potential analysis

The voltage of the external resistor was continuously monitored by a data-logger (ADC-16, Pico technology, UK) and recorded by a linked computer. The current was calculated by Ohm's Law. For polarization and power density analysis, the resistor was gradually alternated from disconnection to 0.1 Ω (nearly short circuit). After each resistance change, the cell was stabilized at least 10 min to allow the microbial adaptation [17]. The system resistance and the maximum power output were calculated from polarization curve and power density curve, respectively. In order to facilitate the comparison of MFC–SSC with SSC, current value was used as the *X*-axis instead of current density. For potential analysis, a saturated calomel electrode (SCE, 0.242 V vs. NHE, 25 °C) was placed closely to each electrode, and a UT-33B digital voltmeter was used to measure the electrode potential.

2.3. Calculation of microbial fuel oxidation and electron generation efficiency

To measure the anodic microbial fuel oxidation and electron pumping efficiency, the external resistor was fixed at 1000 Ω, and the MFC was operated in batch mode. When the performance of each batch got steady, it was refilled with fresh medium for the next operation.

5 mL sample were taken from the medium at 0 and 24 h, which were then filtered with 0.22 μm millipore filters and diluted to 1/3 for COD (chemical oxygen demand) measurements. COD was measured by potassium dichromate photometric method with a HATO CTL-12 COD analyzer (Chengde HATO environmental instrument Co., Ltd, China) at 600 nm. The resistor voltage was also monitored to get the current data, which was then converted into the numbers of electrons by integral operation. The COD values were also converted into the equal numbers of electrons by a 1:8 ratio because oxidation of 1 mol acetate to H_2O and CO_2 gives 8 mol electrons. The microbial oxidation efficiency (MOE) was defined as the oxidation rate of organic substrate (acetate in this study) by anodic microorganisms, which was calculated by measuring the decrease of acetate per unit time. The anodic coulomb efficiency was calculated basing on the ratio of the electrons in the real circuit and the equivalent electrons of COD.

3. Results and discussion

3.1. Power generation in MFC, sterilized MFC–SSC and MFC–SSC

The polarization and power density curves of MFC, sterilized MFC–SSC and MFC–SSC were shown in Fig. 1. The OCV of MFC–SSC was 1208 mV, which was nearly double of the value in sole MFC (665 mV). The system resistance of MFC–SSC (120 Ω) was a little higher than that of MFC (99 Ω), which was due to SSC itself has an internal resistance of 20 Ω under light. The maximum power density of MFC–SSC was 19 W m^{-3}, much higher than that of MFC (7.5 W m^{-3}), indicating a great improvement of electron transfer efficiency by incorporation of SSC into MFC.

It should be noticed that the OCV of MFC–SSC closely approximated the sum of MFC (665 mV) and SSC (600 mV), and its internal

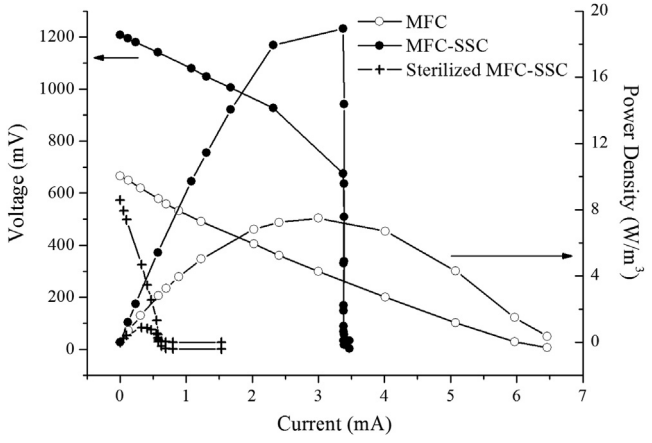

Fig. 1. Polarization and power density curves of MFC, MFC–SSC and sterilized MFC–SSC.

resistance nearly equaled to the sum of MFC (99 Ω) and SSC (20 Ω) under light. So, there arise a question that whether the MFC–SSC is the simple summation of MFC and SSC. In order to clarify this question, we did a control experiment with a sterilized anode MFC and a SSC. The OCV of sterilized MFC–SSC was about 580 mV, similar to SSC itself. And its internal resistance was as large as 900 Ω, much higher than that of MFC or MFC–SSC. Consistently, the maximum power density was only 0.9 W m^{-3}, much lower than that of MFC or MFC–SSC. It was very clear that both the power output and the internal resistance of MFC–SSC didn't equal to the sum of those in MFC and sterilized MFC–SSC. The effect of electro-oxidation of SSC was much weaker than the bio-oxidation of MFC. So, it is sure that MFC–SSC was not a simple summation of MFC and SSC. Obviously, the SSC in sterilized MFC–SSC couldn't make effective electron transfer, and only it cooperated with the anodic microorganisms could realize a rapid electron transfer.

Notably, the polarization and power density curves of MFC–SSC sharply dropped when the current reached the limiting current of SSC at about 3.4 mA. That value was lower than the maximum current of MFC (about 6.5 mA), which indicated the incorporation of SSC did not bring an overload on the bio-anode of MFC. The limiting current of SSC (3.4 mA) was higher than the output current (3.1 mA) of MFC when it reached its maximum power output. So, MFC was considered to be able to function under its most efficient condition when it was united with a SSC to output a maximum power density. It was believable that the SSC used in this work was compatible with the MFC, which was the most essential precondition for achieving a higher power output in MFC–SSC.

3.2. Anodic potential analysis

The anode potential correlated with the electrode reactions and reflected the electron balance states between the anode and the external circuit. When a cell run in the open circuit, electrons would accumulate at the anode, resulting in a low anodic potential. When the current increases, the anodic potential shifts to a more positive value and then established a new balance. As shown in Fig. 2, the anodic potential of MFC gradually increased from −457 mV to −357 mV vs. SCE from open circuit to nearly short circuit. When the current exceeded 5 mA, it was difficult to record the exact values of anodic potential, because it was much more difficult for the electrode potential to get steady under higher current. That also suggested it was more and more difficult for anodic microorganisms to "pump" enough electrons from the oxidation of substrate to establish a balance state, and the anodic reaction equilibrium might be broken near this current value. So, for anodic microorganisms, there should be a limiting current in the cell, which was principally the upper limit of microbial capability.

It was observed that the limiting current of MFC–SSC was about 3.4 mA (Fig. 2), which was also the limiting value of SSC. Below the limiting current value, the anodic potentials of MFC–SSC overlapped those of MFC, indicating the thermodynamics of the anodic reactions were unaffected by the SSC. When the MFC–SSC reached the maximum current of 3.4 mA, any adjustment on the circuit couldn't bring on the continue increase of the current. Simultaneously, the anodic potential kept stable around −415 mV. In fact, the anodic potential of MFC–SSC slightly fluctuated during the whole experimental process, which concentrated at -440 ± 20 mV vs. SCE (with a relative deviation about ±4.5%). This anodic potential range was consistent with that of the previously-reported MFCs, which used acetate as the electron donor and inoculated mixed strains at the anode [18].

The comparison of anodic potentials in MFC and MFC–SSC indicated the addition of SSC didn't affect the thermodynamics of anodic reactions, and it only improve the kinetics of microbial reactions. As long as we keep the anodic microbial reactions stable, the anodic electrons output could be maximized by introducing a SSC into a MFC.

3.3. Anodic electron transfer efficiency in MFC–SSC

According to the current and electric quantity data (Fig. 3), the current of the MFC–SSC maintained near 1.0 mA, while it was only 0.4–0.5 mA in the MFC. Electric quantity had an approximate linear accumulation with a rate of 0.037 mmol h^{-1} in MFC–SSC, as compared with 0.018 mmol h^{-1} in MFC. For comparison, Table 1 summarized the total quantities of transferring electrons, the quantities of oxidized organic substrate, as well as the microbial oxidation efficiency (MOE) and coulomb efficiency. The COD of the anodic medium in MFC decreased from 1641 mg L^{-1}–1421 mg L^{-1} by 13.4% within 24 h, while it significantly decreased from 1593 mg L^{-1}–842 mg L^{-1} by 47.1% in MFC–SSC. The MOE significantly increased from 0.0571 mmol h^{-1} in MFC to 0.195 mmol h^{-1} in MFC–SSC, indicating a great promotion of anodic oxidation efficiency. All those results supported that the anodic oxidation rate of MFC–SSC was significantly improved, so to generate more electrons per unit time to be transferred in the circuit and ultimately realize an enhanced engineering of the system.

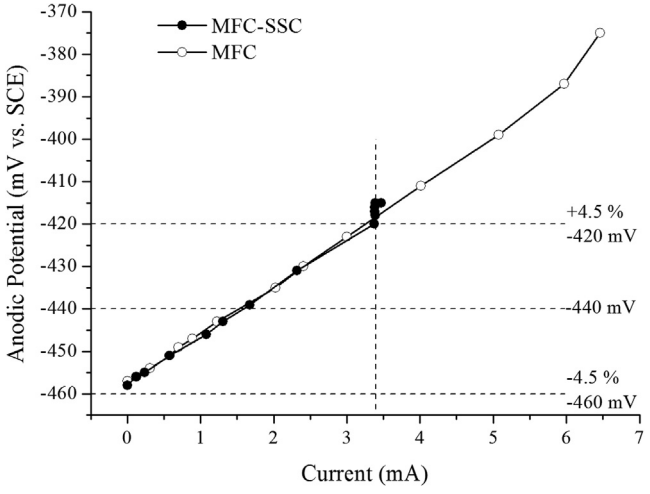

Fig. 2. Electrode potentials of microbial anode in MFC and MFC–SSC.

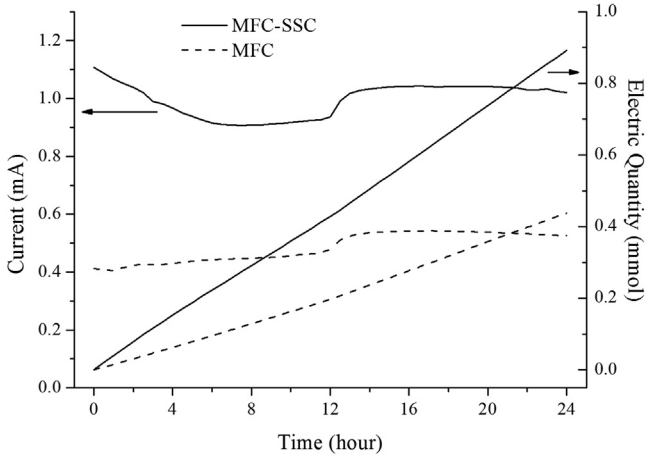

Fig. 3. Current and electric quantity of MFC and MFC–SSC in 24 h.

Table 1
Quantity of anodic organic fuel oxidation and transferring electrons, calculated MOE and coulomb efficiency.

	Acetate oxidation quantity (mmol)	System electron quantity (mmol)	MOE (mmol h^{-1})	Coulomb efficiency
MFC	1.37	0.438	0.0571	3.99%
MFC–SSC	4.68	0.892	0.195	2.38%
Relative percentage	341.6%	203.6%	341.6%	–

3.4. Mechanisms of promoted electron transfer efficiency in MFC–SSC

The MFC–SSC was demonstrated as a cooperating system of MFC and SSC with much higher electron transfer efficiency than either sole MFC or SSC. In fact, the SSC itself didn't offer electrons to the whole MFC–SSC system, and it only elevated the electrons' energy. All electrons flowing in the circuit were originated from the anodic microorganisms. So, the improved power output was the cooperating effects of MFC and SSC, which two behaved different working mechanisms in the integrated MFC–SSC system. The bio-oxidation on anode of MFC supplied electrons, and then SSC converted light energy to electric energy to form a build-in electric field and drive the electrons transfer.

In the built-in electric field of SSC, positive holes and negative electrons were generated at its two terminals, respectively. The positive terminal was connected to the bio-anode, which rapidly neutralized electrons transferred from the anode. That forced the anodic microorganisms to "work harder" to guarantee the electron supply, which eventually resulted in enhanced dynamics of anodic bio-oxidation and reflected by an increase in MOE value.

By analyzing the anodic potentials, we can find the anodic potential of MFC–SSC was decided by the anodic microorganisms and was unaffected by the SSC. In fact, the negative or the positive terminal of a SSC itself does not have an absolute potential value. It only generates a potential difference by photoelectric conversion. Therefore, since the output voltage of SSC was about 600 mV, the electron potential at the negative terminal of SSC decreased by the same value in MFC–SSC. The elevated electric energy was then consumed by the additional resister and behaved as a higher power output in this study.

3.5. Discussion on the compatibility of SSC and MFC

The compatibility of MFC and SSC was very important for the improvement of the whole cell system. In MFC–SSC used in this study, the limiting current of SSC was lower than the maximum current of the MFC, so the incorporation of SSC would not exert an overload on the bio-anode and could keep the thermodynamics of the anodic reactions stable. Also, the limiting current of SSC was a little higher than the output current of MFC when it realized the maximum power output. So, the anode of MFC functioned under its most efficient state in MFC–SSC, and wasn't limited by the SSC. When the limiting current of SSC was equal to the output current of MFC at its maximum power output point, the SSC was believed to match the most efficient condition of MFC, and could ensure the MFC work efficiently in the MFC–SSC.

Generally, the limiting current of the SSC should be higher than the current value of MFC when it outputted the maximum power and lower than the maximum current of the MFC, which was to guarantee the electrons produced from the microbial oxidation can be transferred by SSC as rapid as possible, and simultaneously to avoid the thermodynamic equilibrium of reactions involved by anodic microorganisms being destroyed by the SSC.

4. Conclusions

A SSC was combined with a traditional MFC to improve the cell performance. Results from this study demonstrated that electrons transferred from the anodic microorganisms were indeed promoted by the SSC without influencing the anodic microbial reactions. In the MFC–SSC, electrons generated by anodic bio-oxidation were transferred to SSC and then the electron energy was elevated by SSC's photoelectric conversion, such cooperation of MFC and SSC improved the electron transfer efficiency in the MFC–SSC. As a result, both the power output and the anodic substrate oxidation efficiency were significantly improved. The MFC–SSC has applicable potentials in solar energy utilization and environmental remediation.

Acknowledgments

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